

SUPPORTING INFORMATION

Ru single atoms and nanoparticles on carbon nanotubes as multifunctional catalysts

Diana M. Fernandes,^{1,*} Mariana Rocha,¹ Camila Rivera-Cárcamo,² Philippe Serp², Cristina Freire¹

- 1 REQUIMTE/LAQV, Departamento de Química e Bioquímica, Faculdade de Ciências da Universidade do Porto, Rua do Campo Alegre s/n, 4169-007 Porto, Portugal
- 2 LCC-CNRS, INPT, 205 route de Narbonne, 31077 Toulouse Cedex 4, France

* **Corresponding author:** Diana M. Fernandes, Email: diana.fernandes@fc.up.pt

1. Experimental

1.1. Material preparation

Carbon nanotube synthesis:¹ An AlFeCoO_4 catalyst was reduced in a fluidized bed reactor under a nitrogen (225 mL min^{-1}) and hydrogen (150 mL min^{-1}) flow at $650 \text{ }^\circ\text{C}$. After the reduction step, the ethylene flow was adjusted to 225 mL min^{-1} for 30 min to produce CNT. The CNT were recovered and then purified using an aqueous solution (50 vol% H_2SO_4) under reflux at $140 \text{ }^\circ\text{C}$ for 3 h. The acidic solution was then filtered and the solid washed with distilled water. The resulting solid was dried in an oven at $80 \text{ }^\circ\text{C}$ overnight. A portion of purified CNT was then functionalized with HNO_3 under reflux at $140 \text{ }^\circ\text{C}$ for 3 h. The acidic solution was filtered and washed with distilled water. The resulting solid was dried in an oven at $80 \text{ }^\circ\text{C}$ overnight to produce functionalized CNT (CNT).

1.2. Physicochemical characterization

TEM and HR-TEM analyses were performed at the “Centre de microcharacterisation Raimond Castaing, UMS 3623, Toulouse” by using a JEOL JEM 1011 CX-T electron microscope operating at 100 kV with a point resolution of 4.5 \AA and a JEOL JEM 1400 electron microscope operating at 120 kV. The high-resolution analyses were conducted by using a JEOL JEM 2100F equipped with a field emission gun (FEG) operating at 200 kV with a point resolution of 2.3 \AA and a JEOL JEM-ARM200F Cold FEG operating at 200 kV with a point resolution of $> 1.9 \text{ \AA}$.

XPS measurements were performed on a Thermo $\text{K}\alpha$ spectrometer working at a base pressure of 5×10^{-9} mbar and equipped with a monochromatic Al $\text{K}\alpha$ X-ray source (1486.7 eV). The spectra presented here were recorded with a Pass Energy of 20 eV. The data were processed with CasaXPS using Gaussian-lorentzian combinations and a Shirley background.

Scofield photoionization cross-sections² corrected for the transmission function of the analyser and the analysis depth were used for quantifications.

1.3. ORR and OER electrochemical tests

1.3.1. Materials and solvents

For the electrochemical studies, the following reagents and solvents were used: potassium hydroxide (KOH, 99.99 %, Sigma-Aldrich), platinum nominally 20 % on carbon black (Pt/C 20 wt%, HiSPEC® 3000, Alfa Aesar), Nafion (5 wt.% in lower aliphatic alcohols and water, Aldrich), isopropanol (99.5 %, Aldrich), methanol (anhydrous, VWR) and hydrogen peroxide solution (30 wt.% in water, ACS reagent, Sigma Aldrich). Ultrapure water (18.2 MΩ cm at 25°C, Millipore) was used throughout the experiments.

1.3.2. Electrode cleaning process

Before modification, a cleaning procedure was performed to the RDE with diamond polishing pastes of 6, 3 and 1 μM (Buehler) on a microcloth pad (BAS), followed by washing with ultra-pure water (18.2 MΩ cm at 25°C, Millipore). For the RRDE, the cleaning procedure was performed only with 0.3 μm alumina powder (MicroPolish Alumina, Buehler) in order to prevent damage of Pt ring.

1.3.3. ORR performance

Both the CV and LSV measurements were performed between $E_p = 0.26$ and 1.46 V vs. RHE at 0.005 V s⁻¹. Additionally, rotation speeds in the range 400 - 3000 rpm were used for the LSV experiments. For the chronoamperometry (CA) tests a rotation speed of 1600 rpm for 20 000 s at a potential = 0.55 V vs. RHE was used. Tolerance to methanol was assessed by CA at $E = 0.55$ V vs. RHE and 1600 rpm for 2500 s.

The effective ORR current was obtained by subtracting the current obtained in N₂-saturated electrolyte by that obtained in O₂-saturated.

Even though the potential were measured against the Ag/AgCl reference electrode these were converted to the reversible hydrogen electrode (RHE) using the Eq. 1 for a proper comparison with the literature results.

$$E_{(\text{RHE})} = E_{(\text{Ag}/\text{AgCl})} + 0.059 \text{ pH} + E_{(\text{Ag}/\text{AgCl})}^{\circ} \quad (\text{Eq. 1})$$

where $E_{(\text{RHE})}$ is the potential vs. RHE, $E_{(\text{Ag}/\text{AgCl})}^{\circ} = 0.1976 \text{ V}$ (25 °C) and $E_{(\text{Ag}/\text{AgCl})}$ is the potential measure vs. Ag/AgCl.³

Onset potential (E_{onset}) is defined as the potential at which the reduction of O₂ begins. According to literature the E_{onset} can be determined by different methods³⁻⁵ and is generally assume as the potential at which the ORR current is 5% of the diffusion-limiting current density or it can be calculated as the potential at which the slope of the voltammogram exceeds a threshold value ($j = 0.1 \text{ mA cm}^{-2}\text{V}^{-1}$).^{4, 5} Here we considered the first method.

The kinetic parameters and the number of electrons transferred per O₂ molecule (n_{O_2}) in the oxygen reduction reaction were determined using the following Koutecky-Levich equations:

$$\frac{1}{j} = \frac{1}{j_L} + \frac{1}{j_k} = \frac{1}{B\omega^{1/2}} + \frac{1}{j_k} \quad (\text{Eq. 2})$$

$$B = 0.2 n_{\text{O}_2} F (D_{\text{O}_2})^{2/3} \nu^{-1/6} C_{\text{O}_2} \quad (\text{Eq. 3})$$

Here, j is the current density measured, j_L and j_k are the diffusion-limiting and kinetic current densities, ω is the angular velocity, F is the Faraday constant (96 485 C mol⁻¹), D_{O_2} is the O₂ diffusion coefficient ($1.95 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$), ν is the electrolyte kinematic viscosity ($0.008977 \text{ cm}^2 \text{ s}^{-1}$), C_{O_2} is the O₂ bulk concentration ($1.15 \times 10^{-3} \text{ mol dm}^{-3}$). For rotation speeds in rpm is adopted a constant of 0.2.⁶

Tafel plots were obtained after the measured LSV currents were corrected for diffusion to yield the corresponding kinetic current values. The j_L parameter, obtained through the combination of Eq. 2 and 3, was used to make the mass transport correction. The values of j_k obtained were normalized for the total deposited mass of EC.

Rotating ring disk electrode (RRDE) measurements in O₂-saturated KOH solution were also performed in order to obtain a more in-depth insight of the ORR electrocatalytic activity of the ECs. The H₂O₂ yields were determined from the ring and disk currents (i_R and i_D , respectively), and the current collection efficiency of the Pt ring ($N = 0.25$, in this case) using Eq. 1:⁷

$$\% \text{ H}_2\text{O}_2 = 200 \times \frac{i_R / N}{i_D + i_R / N} \quad (\text{Eq. 4})$$

1.3.4. OER performance

OER studies were performed in N₂-saturated alkaline electrolyte, 0.1 M KOH solution purged with N₂ for at least 30 min before the measurement. LSVs were obtained by sweeping the potential from 0.87 to 1.87 V (vs. RHE) with a scan rate of 0.005 V s⁻¹ at 1600 rpm. All presented LSV tests were performed with i_R -compensation, via previous calculation of the uncompensated resistance (Ru) of the circuit by using i -interrupt approach, and finally, applying an i_R -compensation value equal to 0.90×Ru to the LSV measurement. Tafel slopes were determined by linear fitting of LSV data to the following equation:

$$\eta = a + b \times \log |j| \quad (\text{Eq. 1})$$

where η is the overpotential, b is the Tafel slope, and j is the current density.

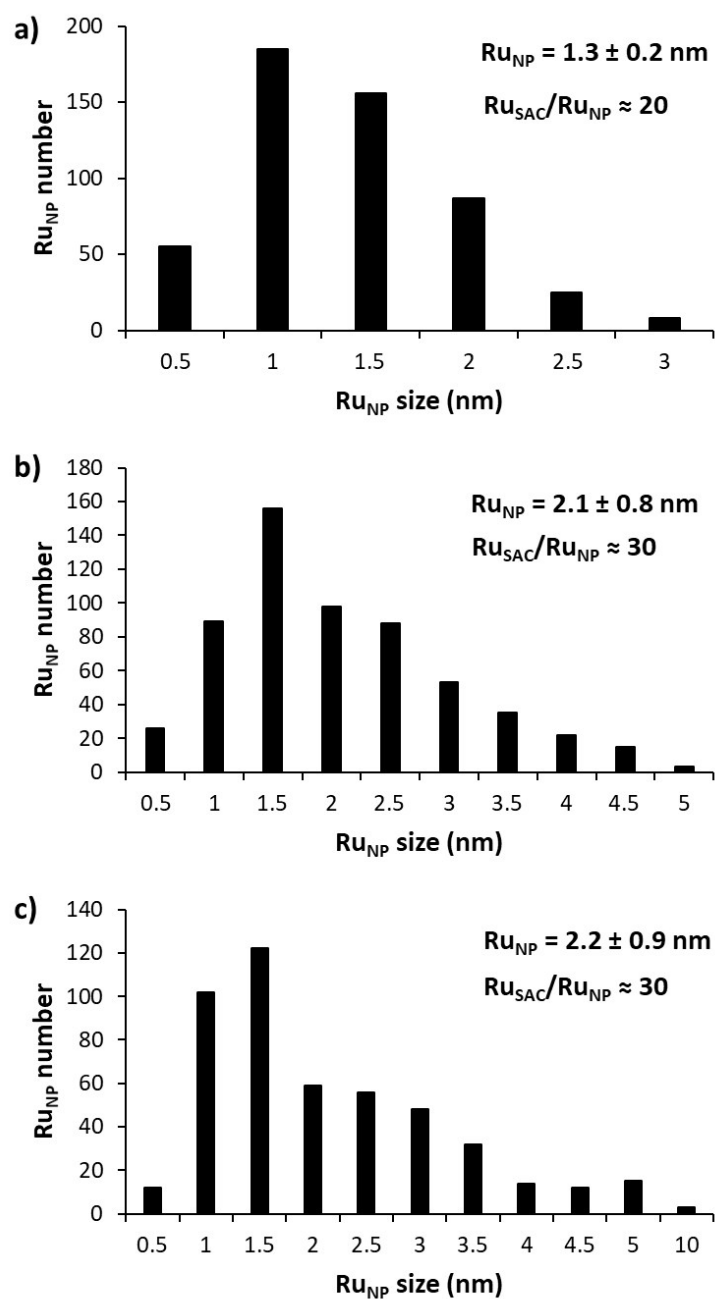


Figure S1. Histograms of Ru_{NP} size distribution, mean Ru_{NP} size and Ru_{SAC}/Ru_{NP} ratio of: a) Ru/CNT; b) Ru/CNT_{4NA} (after 4NA catalytic reduction); and c) Ru/CNT_{4NP} (after 4NP catalytic reduction).

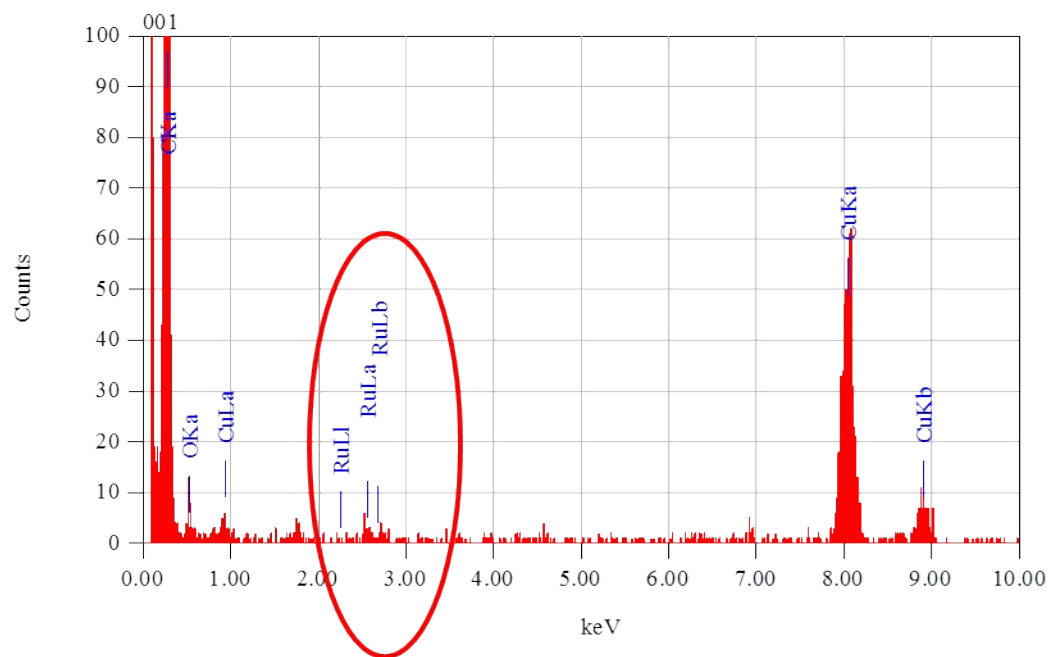
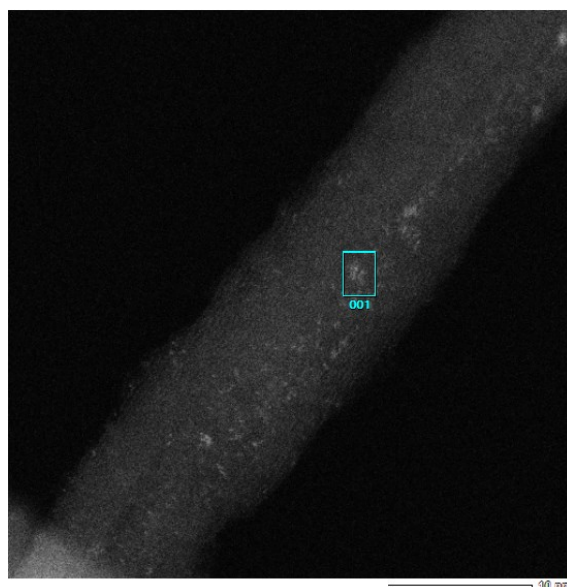
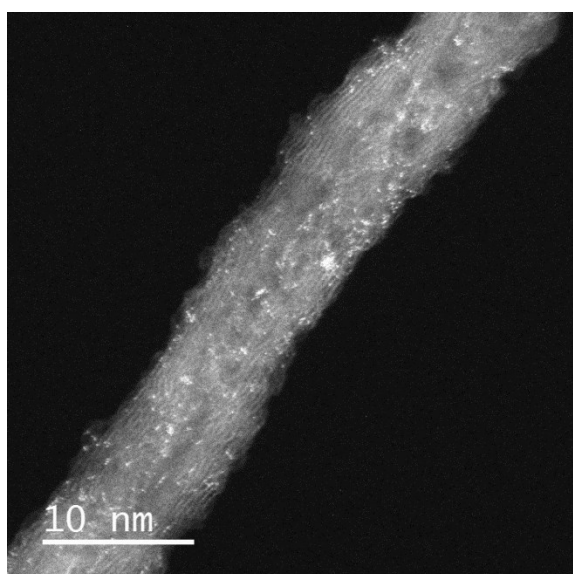


Figure S2. STEM-HAADF analyses of a zone containing mainly Ru_{SAC} and respective EDX analysis.

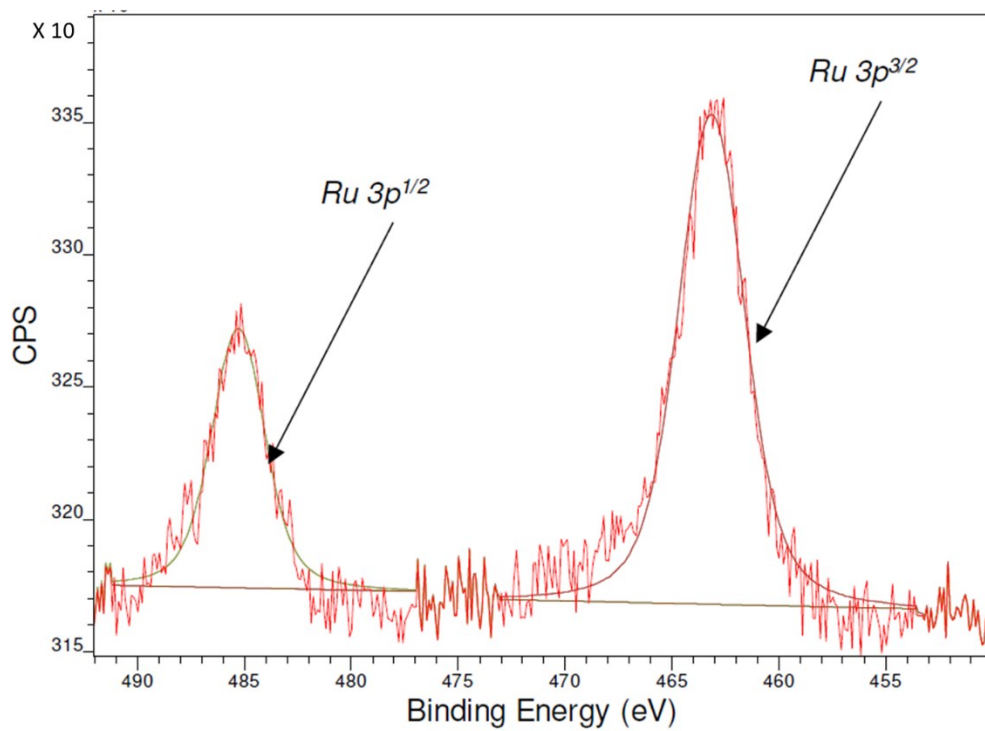


Figure S3. High-resolution XPS spectrum of Ru 3p of the Ru/CNT catalyst.

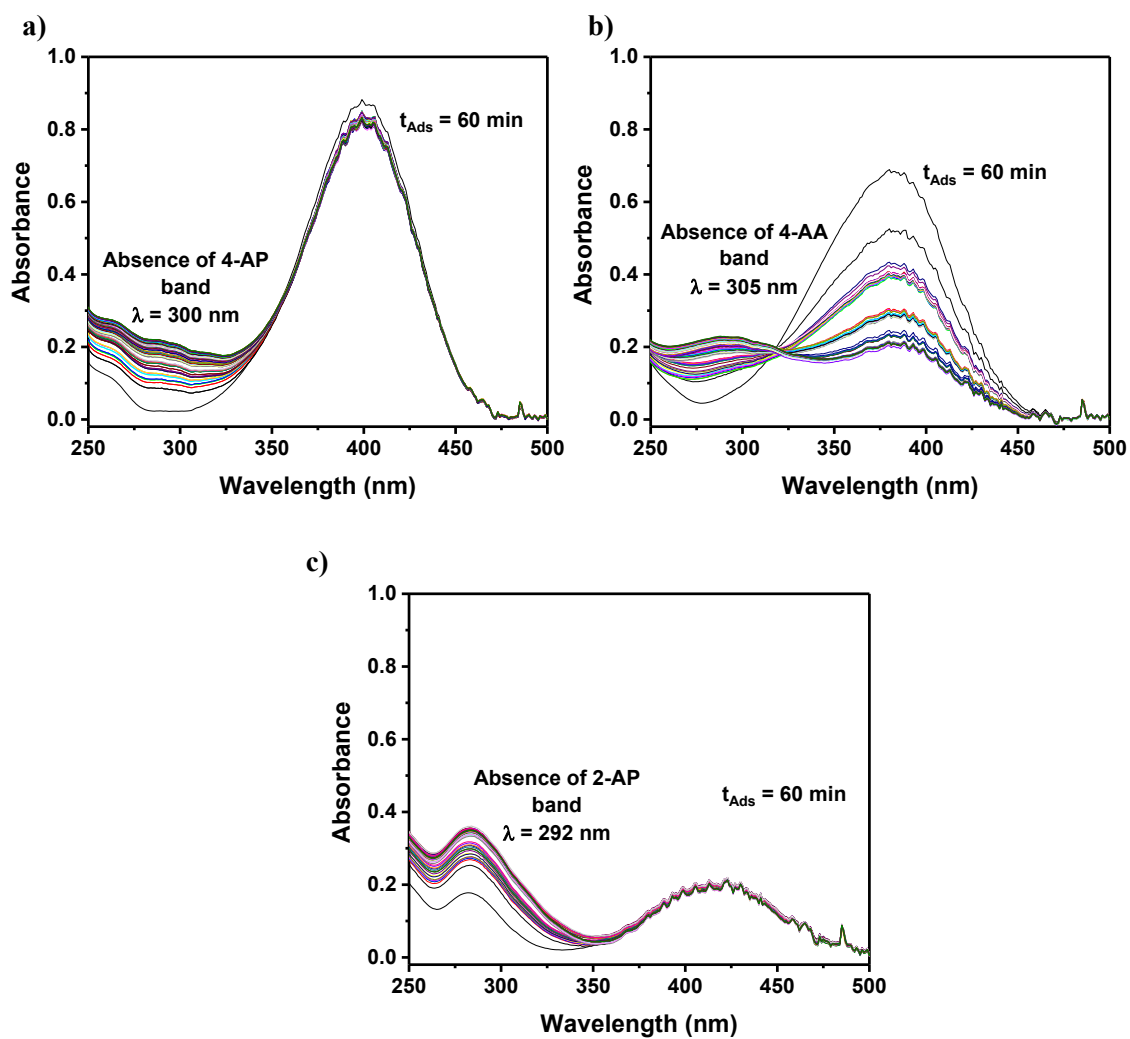


Figure S4. UV-Vis spectra of the nitroarenes adsorption tests onto Ru/CNT material (conditions: $|\text{nitroarene}| = 0.05 \text{ mM}$; $|\text{Ru/CNT}| = 1 \text{ mg mL}^{-1}$; adsorption time = 60 min): a) 4-NP, b) 4-NA and c) 2-NP.

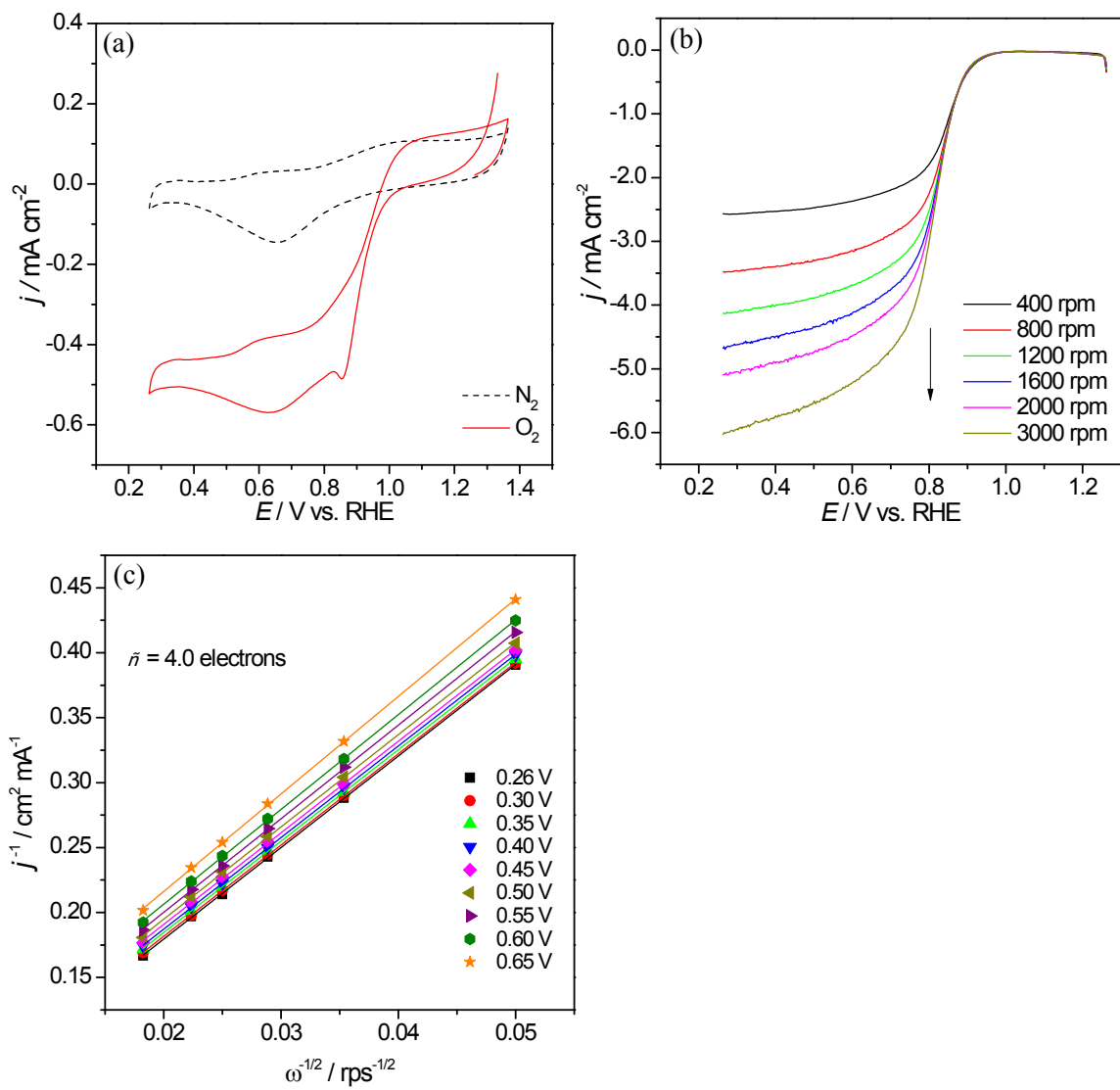


Figure S5. CVs of commercial Pt/C (20 wt %) modified electrode in N₂-saturated (dash line) and O₂-saturated (full line) 0.1 mol dm⁻³ KOH solution at 0.005 V s⁻¹ (a), ORR polarization curves at different rotation rates in O₂-saturated 0.1 mol dm⁻³ KOH solution at 0.005 V s⁻¹ (b) and the corresponding KL plots (c).

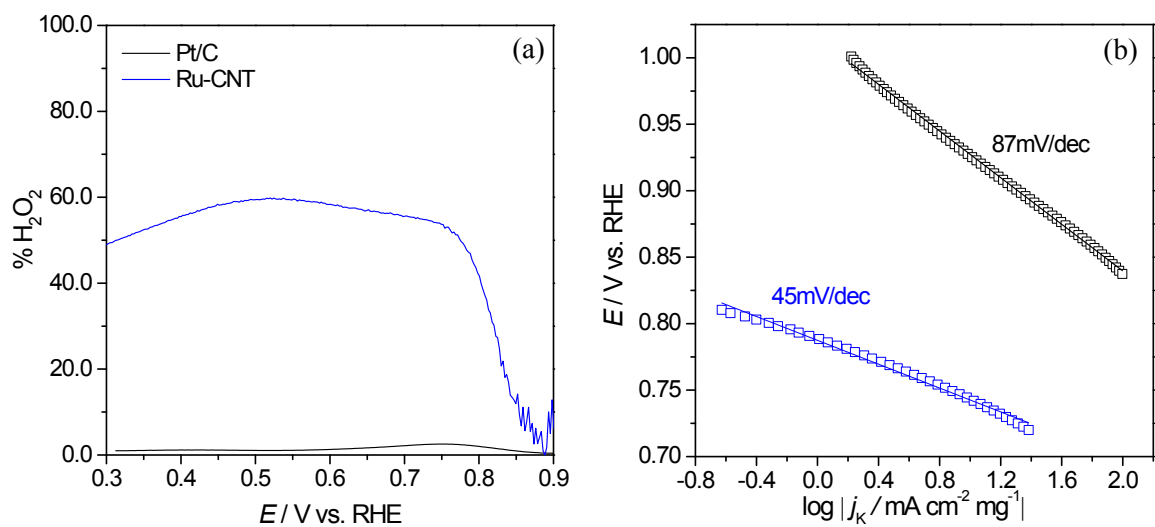


Figure S6. Estimated percentage of H_2O_2 formed (a) and ORR Tafel plots (b) of Ru/CNT (blue) and Pt/C (black) obtained from LSV curves in O_2 -saturated 0.1 mol dm^{-3} KOH solution, at 1600 rpm and $\nu = 0.005 \text{ V s}^{-1}$.

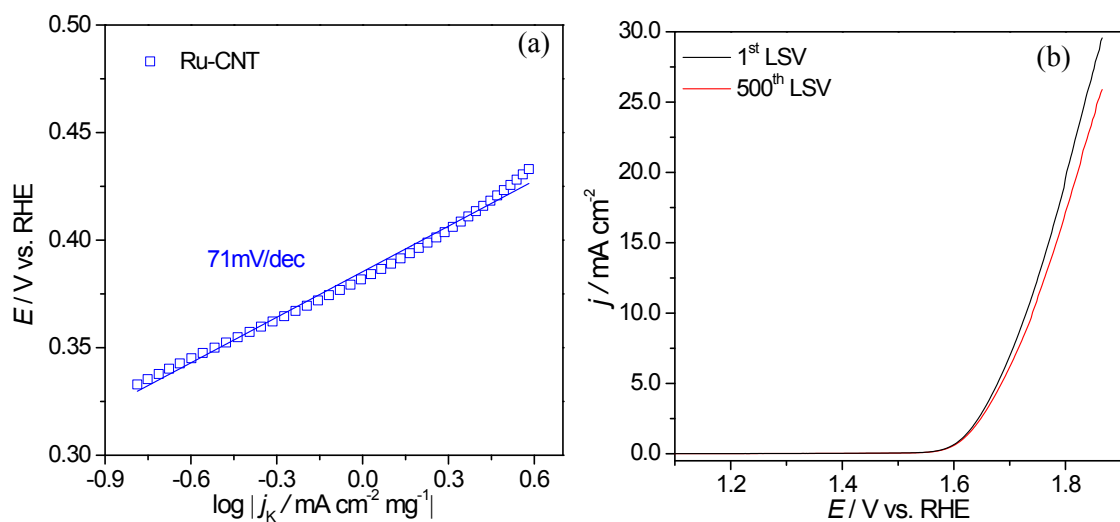


Figure S7. OER Tafel plot (a) and stability test (b) of Ru/CNT in O_2 -saturated KOH, at 1600 rpm and $\nu = 0.005 \text{ V s}^{-1}$.

References

1. R. C. Contreras, B. Guicheret, B. F. Machado, C. Rivera-Carcamo, M. A. C. Alvarez, B. V. Salas, M. Rutttert, T. Placke, A. F. Reguillon, L. Vanoye, C. de Bellefon, R. Philippe and P. Serp, *J. Catal.*, 2019, **372**, 226-244.
2. J. H. Scofield, *J. Electron Spectrosc. Relat. Phenom.*, 1976, **8**, 129-137.
3. C. Freire, D. M. Fernandes, M. Nunes and V. K. Abdelkader, *ChemCatChem*, 2018, **10**, 1703-1730.
4. N. Daems, X. Sheng, I. F. J. Vankelecom and P. P. Pescarmona, *J. Mater. Chem. A*, 2014, **2**, 4085-4110.
5. X. J. Zhou, J. L. Qiao, L. Yang and J. J. Zhang, *Adv. Energy Mater.*, 2014, **4**, 25.
6. G. Tuci, C. Zafferoni, A. Rossin, A. Milella, L. Luconi, M. Innocenti, L. T. Phuoc, D. V. Cuong, P. H. Cuong and G. Giambastian, *Chem. Mat.*, 2014, **26**, 3460-3470.
7. D. M. Fernandes, P. Mathumba, A. J. S. Fernandes, E. I. Iwuoha and C. Freire, *Electrochim. Acta*, 2019, **319**, 72-81.